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Title: INTRODUCTION TO THE TIME SCALE PROBLEM

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Introduction to the time scale problem

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ABSTRACT

As motivation for the symposium on extended-scale atomistic methods, I briefly discuss the time scale problem that plagues molecular dynamics simulations, some promising recent developments for circumventing the problem, and some remaining challenges.

Keywords: kinetic Monte Carlo, hyperdynamics, temperature accelerated dynamics, parallel-replica dynamics, dimer method

INTRODUCTION

The nanoscale is an exciting regime for practitioners of atomistic simulation techniques, because in the last few years there has been a crossing of the length scales accessible to simulation and experiment. The size of a nanofeature that can be directly synthesized and probed experimentally has continued to decrease, while simulation sizes have increased. Using parallel computers, it is now fairly easy to simulate millions of atoms using molecular dynamics, and it is possible to reach a billion atoms if desired. Thus, in many cases, a direct simulation of an entire nanoscale device can now be performed.

In contrast to this pleasant length-scale situation, the *time* scales accessible to molecular dynamics simulation remain a serious problem. Because the classical equations of motion must be integrated sequentially using time steps on the order of one femtosecond (chosen to be more than an order of magnitude shorter than the shortest atomic vibrational period), reaching a simulation time of even a single microsecond is extremely difficult. Increasing computer speeds will improve this situation, but not in a qualitative way. Ten years from now, optimistically assuming Moore's law continues to hold, we will still not be close to reaching one millisecond, which is still shorter than the time scale for many experimentally relevant processes in the fabrication, application, or degradation of nanoscale devices. For example, in the deposition of a thin film, each monolayer of material is deposited in a time on the order of one second, and the morphology of the resulting film is strongly affected (often dominated) by diffusive events occurring on this time scale.

For a broad class of systems, the dynamics on this longer time scale can be characterized by infrequent events – typically thermally activated processes, as in the film growth example mentioned. A schematic illustration of this type of system is shown in Fig. 1; the system is trapped in a potential basin for a large number of vibrational periods. For this type of system there are ways around the time-scale problem. A now-standard approach is the kinetic Monte Carlo method, which can reach extremely long times once a few assumptions are made. This is briefly described below. More recently, there have been developments in methods that show promise for reaching long time scales without some of the approximations in kinetic Monte Carlo, and developments of associated tools for efficiently finding saddle points [1]–[4] and transition paths [4], [5], including quantum effects [6], etc.

Although it was claimed above that the length scale problem is largely solved for the nanoscale realm, this is not true if we ask for simulations that simultaneously address relevant lengths and time, since, in general, the methods described below are still too expensive for this, and most of them exhibit a computational scaling that grows superlinearly with the system size, N. Improving this scaling (to achieve N-scaling, ideally) is a remaining challenge. Until this is achieved, it will be important to combine these methods with the recently developed length scale methods such as the quasicontinuum method [7], [8] or coarse-grained molecular dynamics [9], [10] . In this symposium we will assess the state of the art of this family of time- and length-scale tools and seek ways to extend and combine them. Here I very briefly describe kinetic Monte Carlo and a few of the time-scale methods developed more recently.

TIME-SCALE METHODS

In the kinetic Monte Carlo (KMC) method, developed over the last 25 years [11]–[16], the system starts in some state, typically with atoms assigned to lattice positions. Equations of motion are never directly evolved. Instead, we focus on the fact that a set of escape pathways connect this state to neighboring states. The key requirement in KMC is to specify these escape paths and the rate constant for each one. Given this set of rates,

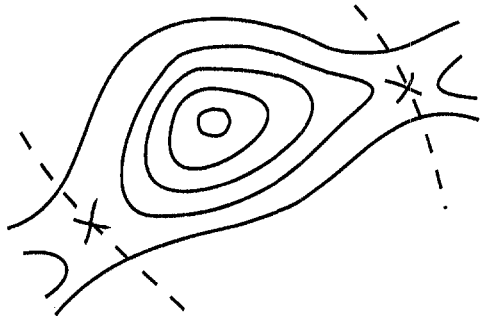

Figure 1: Schematic illustration of a potential energy basin in which the system is trapped (lines are constant-energy contours). Infrequent events (activated processes) correspond to the system finding its way out of this basin to an adjacent one. The time scale problem is that with molecular dynamics, we can only afford to follow about a million vibrations, while (depending on the system and temperature) the system may remain trapped for far longer.

a simple stochastic algorithm [11], [12] is employed to advance the time and to choose a neighboring state to which the system is moved, after which the procedure is repeated. The rate constants for the possible moves out of each state might be approximated by a few additive parameters, or computed more accurately using transition state theory to make a rate catalog [13], perhaps even using first-principles calculations [15]. The KMC approach is very powerful, and can typically reach time scales many orders of magnitude greater than molecular dynamics, since the system advances to a new state in less computer time than would be expended in molecular dynamics to advance by a single integration step. The difficulty in the KMC approach is knowing all the possible mechanisms available to the system for escaping from the present state. In recent years, it has become clear that these mechanisms can be surprisingly complex, often involving many atoms and sometimes going off-lattice, even in relatively simple systems. Whether these unexpected mechanisms are important to the long-time dynamical evolution depends on the system, and remains to be proven in general, but their very existence provides a clear motivation to develop methods that make no *a priori* assumptions about the mechanisms. Recent developments aimed at this goal are sketched in the following. These new methods can be used directly to follow long-time dynamics or, in principle, used to scan for unexpected mechanisms to provide improved rate catalogs for KMC, since KMC will always be substantially faster.

In the accelerated dynamics methods, the basic concept is to perform actual dynamics on the system of atoms, allowing it to escape from each basin in any way it wants (perhaps via a complex concerted mechanism), but to coax it to escape more quickly than it otherwise would. The key is to realize that the exact details of the vibrational motion need not be reproduced. Building on transition state theory [17], it is possible to design methods that sacrifice information about these vibrations and gain, in exchange, more rapid escape from the basin without corrupting the relative escape probabilities. Temperature accelerated dynamics (as well as the dimer method described below) builds on the principles of harmonic transition state theory, in which nearly all the information about the rates is contained in the saddle points for the escape paths (the X's in Fig. 1), but in general, it is the flux across the dividing surface (dashed line in Fig. 1) that must be correctly described. These methods (hyperdynamics, parallel replica dynamics, and temperature-accelerated dynamics) are described elsewhere in these proceedings [18], [19] and, along with the dimer method discussed below, have been recently reviewed [20].

In hyperdynamics [21], [18], one designs a positive bias potential which, when added to the original potential, has the effect of making the basins less deep. If the bias potential is carefully constructed to be zero at all the dividing surfaces, and does not create correlated dynamical events (e.g., recrossings of a dividing surface), then the dynamics on the biased potential give a proper state-to-state sequence of transitions. The concept of filling in the basin to stimulate more rapid escape is similar to the conformational flooding approach of Grubmüller [22]. In hyperdynamics, the accelerated time becomes a statistical property of the system, estimated as the simulation evolves. Designing effective bias potentials is challenging, and is a subject of ongoing research [20].

In the parallel replica method [23], [18], a replica of the system is placed on a number of processers. Exploiting the properties of the exponential probability distribution for the first-passage time, it is possible to show that by simply accepting whichever event occurs first on any of the processors, and adding the time accumulated on all the processors (after an initial dephasing period), the exact dynamical evolution of the system is obtained. In favorable cases, a full parallel speedup can be obtained, and the method is quite general. For example, Zagrovic et al [24] have recently designed a clever transition detection scheme for the detection of transitions among free-energy basins in a small protein, and applied parallel replica to follow the folding dynamics. Properly applied, parallel-replica makes no transition state theory assumption, and even appears to be applicable to driven systems [25], something that is much harder for other extended-time methods.

The temperature accelerated dynamics (TAD) method [26], [19] utilizes the Arrhenius temperature dependence of the rate constants in harmonic transition state theory. Molecular dynamics simulation is performed at an elevated temperature while the system is confined to its current basin – i.e., every attempted escape is reflected back into the basin. An extrapolation procedure gives a predicted time at which each of these attempted escapes would have occurred at the lower (desired) temperature. With one additional assumption of a minimum preexponential factor, it is possible to say when the high-temperature simulation can be terminated, knowing what escape path the system would have chosen at low temperature (and when). The TAD method is more approximate than hyperdynamics or parallel-replica dynamics, but also appears to give greater boost in most situations. Various enhancements in both the speed [27] and accuracy are now being explored.

The final method I mention is the dimer method [4], [28]–[30]. The "dimer" refers to a two-configuration construction that, by optimizing its orientation, gives the lowest eigenvalue and eigenvector of the Hessian matrix without ever constructing the Hessian [4], [31], [32]. Henkelman and Jónsson have turned this dimer construct into a highly efficient saddle-finding algorithm, in which the dimer follows the lowest eigenvector up the energy trough to the saddle. Recently [28], they have shown that, given a number of dimer searches initiated as random displacements from the basin minimum, they can find enough low-lying saddle points to do an effective "on-the-fly" kinetic Monte Carlo simulation. As in TAD, one exploits the fact that in harmonic transition state theory the escape rate for a given pathway depends purely on saddle point. However, in this dimer-KMC approach, one never needs to run a trajectory. Although it is possible that the random search procedure can miss relevant saddle points, preliminary results indicate that the method is powerful and efficient, and has no problem finding highly concerted mechanisms.

CONCLUSIONS

Recent developments in methods for extending the time scale accessible to atomistic simulations look promising. Already, applications to metallic surface growth [28], [33] have achieved time-scale enhancements of many orders of magnitude (e.g., reaching realistic growth rates in the monolayer per second range [33]). Interesting and challenging problems remain, such as improving the computational scaling with system size, combining time-scale methods with length-scale methods, adapting the methods to other system types (e.g., soft matter), and transferring advanced mechanism information to KMC.

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